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Suppression of the Jahn–Teller effect in nanoparticles: AgCl nanocrystals embedded in KCl matrix

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Abstract. A strong decrease in the g-factor anisotropy was revealed by optically detected magnetic resonance for self-trapped Jahn–Teller holes (both isolated and forming self-trapped excitons) in AgCl nanocrystals embedded into the KCl crystal lattice. This implies a considerable suppression of the Jahn–Teller (J–T) effect in nanoparticles. A rather general mechanism of the suppression of the Jahn–Teller effect in nanocrystals is developed, taking into account the additional deformation field appearing because of the strong vibronic interaction at the interface.

Introduction

In the last decade, nanostructures have been successfully fabricated using self-organization effects common to strained heterosystems [1]. Fabrication of new structures and devices based on anisotropic nanoparticles is of great interest since anisotropic particles can exhibit novel and enhanced properties, compared with those of isotropic spherical particles. Semiconductor nanocrystals have been mainly studied for II–VI semiconductors dispersed in a vitreous matrix [2]. However, nanocrystals can show a common orientation only in a crystalline matrix, as recently demonstrated for CuCl and AgCl nanocrystals embedded in an alkali halide matrix [3–7].

It is well known that the electronic, as well as atomic, structure is considerably changed as the size increases from clusters to small particles and, finally, to a bulk material, through which manifold interesting properties are developed. In this respect, KCl:AgCl seems to be a very promising system for studying these effects. It has long been known that silver ions Ag^+ substitute for alkali ions in silver doped alkali halide crystals. Ultra-violet (UV) light or x-ray irradiation can produce a number of different silver-related point defects. On the other hand, silver halide nanometre- and micrometre-size crystals, i.e. nanocrystals and microcrystals, can be formed in growth of KCl single crystals heavily doped with AgCl, as recently reported in [5–7]. KCl and AgCl have the same face-centred cubic lattice with the lattice constants 0.629 nm and 0.555 nm, respectively. The energy gap are 8.7 eV for KCl and 3.26 eV for AgCl. Thus, AgCl crystals embedded in KCl can be considered as an array of self-organized microcrystals and nanocrystals (quantum dots) in a strained KCl:AgCl heterosystem.

The effects of confinement on shallow centres with Bohr radius comparable with the particle size are well known (see [1–2] for references). The influence of the nanoparticle size on deep level centres and local effects in solids is of fundamental importance, being, however, much less studied to our knowledge. The Jahn–Teller (J–T) effect is one of the basic local effects in solids, rather sensitive to internal fields and variations of the electron–phonon interaction. STH and STE in bulk AgCl are classical J–T systems well studied in bulk AgCl by various radiospectroscopic techniques. Therefore, investigation of AgCl nano- and microcrystal systems embedded in a crystalline matrix seems to be very interesting.

1. Results and discussion

The KCl:AgCl crystals were grown by the Stockbarger method. The silver concentration in the melt was 2%. ODMR at a frequency of 35 GHz and temperature of 1.6 K was detected from the luminescence excited by the UV light of an arc deuterium lamp with appropriate light filters. The microwave power in the cavity of an ODMR spectrometer was modulated at a sound frequency, and the microwave-induced changes in the luminescence intensity were detected using a lock-in detector. The samples (#1, #2 and #3) were cleaved from different parts of the grown crystal and represented transparent single crystals without visible inclusions.

In the present study two types of ODMR spectra have been observed in heavily doped KCl:AgCl which belong the following centres, presented in Table 1:

(i) The STH, STE and SEC in oriented AgCl microcrystals which have the parameters close to those for the bulk AgCl.

(ii) The anisotropic centres with $S = 1/2$ and $S = 1$ ascribed to STH and STE in AgCl nanocrystals and having the parameters which are essentially different from those of bulk AgCl. Similar $S = 1$ centres were ascribed in [6] to STE in AgCl nanocrystals with $L < 10$ nm.

In the 35 GHz ODMR spectra of sample #1 and bulk AgCl the lines of STH, STE and SEC are well resolved due to strong anisotropy of g -factors and relatively large fine structure splitting D . For the ODMR of $S = 1/2$ and $S = 1$ centres in samples #2 and #3 both the anisotropy of g -factors and the parameter D are considerably reduced. Nevertheless we were able to discriminate between the signals of the $S = 1$ and $S = 1/2$ centres since the relative intensities of the ODMR spectra depend on the microwave power and the chopping frequency. The angular variations of ODMR in sample #2 for the rotation in the (110) plane are shown in Fig. 1. Full and dashed lines show the ODMR spectra recorded with the chopping frequencies 80 Hz and 800 Hz, respectively. At higher chopping frequency the signals of the doublet spectrum are more pronounced. The $S = 1/2$ centres dominated in the ODMR spectrum of sample #3.

Observation of bulk-like ODMR in KCl:AgCl can be considered as the direct confirmation of the formation of AgCl microcrystals (apparently of micron size) in KCl matrix. These microcrystals have practically the same properties as bulk AgCl and maintain the orientation of the host KCl lattice. The misorientation of the AgCl microcrystals as estimated from the ODMR spectra is below 5° . Thus ODMR was used as a fingerprint of the embedded AgCl crystals and a confirmation of their high crystallographic quality.

Table 1. Parameters of STH, STE and SEC in bulk AgCl crystals and AgCl micro- and nanocrystals embedded in KCl matrix

Crystal		Centre						Refs.
		STH		STE			SEC	
		g_{\parallel}	g_{\perp}	g_{\parallel}	g_{\perp}	D (MHz)	g	
Bulk		2.147	2.040	2.0216	1.968	−710	1.881	[8]
AgCl	micro-	2.147	2.040	2.020	1.966	−710	1.88–1.90	this work
embedded	nano-	—	—	1.992	1.964	−335	—	[6]
in KCl	crystals	2.016	1.974	1.992	1.965	−335	~1.96	this work

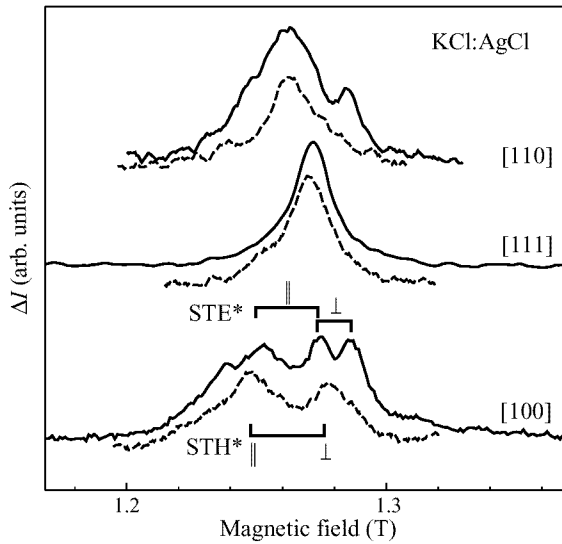


Fig. 1. ODMR in KCl:AgCl sample #2 recorded with microwave chopping frequency $f_{chop} = 80$ Hz (full curves) and $f_{chop} = 800$ Hz (broken curves) for the three principal orientations in the (110) plane. The position of the ODMR lines for self-trapped excitons and self-trapped holes in AgCl nanocrystals are marked by STE* and STH*. Symbols \parallel and \perp denote the centres with the Jahn–Teller axis parallel and perpendicular to the magnetic field, respectively. $T = 1.6$ K; $\nu = 35.2$ GHz; $P_{\text{microwaves}} = 300$ mW.

Although the arguments in favour of the assignment of the ODMR spectra in samples #2 and #3 to AgCl nanocrystals seems to be rather convincing one can not totally exclude that they may be connected to point defects in KCl. Our analysis of the EPR and ODMR spectra showed that the obtained ODMR spectra do not correspond to EPR of any known point defect or STE in KCl.

There exist a direct link between the g -factors of STE and those of STH and SEC. $\vec{g}_{\text{STE}} = (\vec{g}_{\text{STH}} + \vec{g}_e)/2$. This strictly holds for bulk AgCl crystals and AgCl microcrystals (see Table 1). It is natural to suppose that the same is valid for the AgCl nanocrystals. It is seen from Table 1 that g -factors for STH and STE in AgCl nanocrystals satisfy this equation within the experimental error if we suppose that g -factor of SEC remains isotropic in the nanocrystals. In addition, this allows to estimate the g -factor of SEC in AgCl nanocrystals as ca. 1.96 which is much larger than in bulk AgCl. We emphasise that the existence of correlation between g -factors of the $S = 1/2$ and $S = 1$ centres strongly supports their identification as STH and STE in AgCl nanocrystals.

Thus, in AgCl nanocrystals with the size down to 10 nm both the doublet and the triplet ODMR spectra ascribed to STH and STE in nanocrystals were found with the parameters essentially different from STH and STE in bulk AgCl (see Table 1). In bulk AgCl crystals the difference $g_{\parallel} - g_{\perp}$ is 0.107 for STH and 0.054 for STE. In AgCl nanocrystals the respective values are 0.042 and 0.027, i.e. about two times smaller.

The anisotropy of g -factor of the 2E J–T state of STH in the cubic environment is determined by the effective Zeeman interaction and is described by introducing the appropriate electron operators \hat{U}_{θ} and \hat{U}_{φ} in the basis of the 2E state [9].

The average value of the g -factor tends to the isotropic contribution g_1 with a decrease of the strength of the J–T effect because $\langle \hat{U}_{\theta} \rangle \rightarrow 0$ and $\langle \hat{U}_{\varphi} \rangle \rightarrow 0$. Thus the observed

pronounced decrease of the g -factor anisotropy of STH in AgCl nanocrystals implies a considerable suppression of the J–T effect.

We consider a change in the energies of electron and hole states at the nanocrystal interface as a main mechanism governing the JTE in nanocrystals. It should be noted that the energy gap jump of ~ 5 eV from KCl to AgCl occurs at a distance of about 3 Å. This results in a large vibronic coupling constant at the interface. The vibronic coupling at the interface brings about weakening or suppression of the pseudo Jahn–Teller effect in sufficiently small-sized nanocrystals. This results in a decrease or suppression of the anisotropy in the EPR (ODMR) spectra of STH; i.e., the difference $g_{\parallel} - g_{\perp}$ decreases. Since the STE is formed through electron capture by the STH, the anisotropy of the STE g tensor should also decrease or be suppressed. Estimates show that the considered mechanism can account for the reduction of the J–T effect of STH for $L < 10$ nm, which seems to be reasonable for the system under study. The details of the proposed mechanism can be found in [10, 11].

It should be noted that the proposed mechanism of the formation of the internal nanostructure strain field due to the interface vibronic effect is rather general and can be actual for a set of nanostructures and thin films.

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